Indian J. Phys. **78** (9), 1003-1005 (2004)

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NATIONAL JOURNAL

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X-ray diffraction studies of 2-[2'-hydroxy salicylidene 5'-(4''phenyl 2''-thiazolylazo)] benzoic acid

S S Chavan

Department of Chemistry, Shivaji University, Kolhapur-416 004, Maharashtra, India

E-mail sanjaycha2@yahoo.com

Received 17 October 2003, accepted 20 July 2004

Abstract The Schiff base, 2-[2'-hydroxysalicylidene-5'-(4''-phenyl 2'' thiazolylazo)] benzoic acid was prepared by condensing 5'-(4' phenyl 2'-thiazolylazo) salicylaldehyde and 2-amino benzoic acid The purified sample is characterized and has been subjected to X-ray diffractometry to elucidate structural information The structure of the sample is found to be tetragonal belonging to non primitive system The strain broadening effects are also examined and discussed

Keywords Azo compounds, X-ray diffraction

PACS No. 61 10 Nz

Schiff bases containing azo group have received special attention for their biological activities like bacteriostatic [1], anticancerous [2] and other biochemical properties [3, 4]. Heterocyclic ring containing sulphur, nitrogen and or oxygen impart special biological activity to these Schiff bases and their metal complexes[5-8]. Since the enhancement of biological activity and toxicity is generally achieved by complexing these biological active compounds with metal ion [9], it is therefore, of considerable interest and importance to know details about coordinating behaviour of Schiff base ligand. We have attempted here to report the synthesis of one such Schiff base, 2-[2'-hydroxy salicylidene-5'- (4''- phenyl - 2''- thiazolylazo)] benzoic acid and examined for structural properties.

All the chemicals used were E. Merck reagents. 4-phenyl, 2-aminothiazole was prepared according to the method available in literature [10]. 5-(4'-phenyl-2'-thiazolylazo)salicylaldehyde was prepared by diazotization of 4-phenyl 2-amino- thiazole(1g, 0.01 mole) using conc. H_2SO_4 and $NaNO_2$ by following the method reported earlier[11]. The resultant diazonium salt so formed, was consequently coupled with salicylaldehyde (1.28g, 0.01 mole) dissolved in 15 ml aqueous 2N NaOH. The reaction mixture was stirred for 1 h at 0^0C and then allowed to warm slowly at room temperature. The dark brown precipitate formed was filtered, washed with water and recrystallised from ethanol.

2-aminobenzoic acid (2.939 g, 0.02 mole) was dissolved in 15 ml ethanol and was added dropwise to an ethanolic solution of 5-(4'-phenyl, 2'-thiazolylazo) salicylaldehyde (5g, 0.02 mole) dissolved in 50 ml ethanol with constant stirring. The resulting mixture was refluxed for 3-4 h on water bath. After cooling, it was poured into crushed ice, when a pinkish violet coloured compound separated out. It was then filtered, washed and recrystallised from ethanol. The purity of the product was checked by thin layer chromatography.

Colour, yield, melting point and elemental analysis are as follows:

Pinkish violet, yield 58%, Mp.- 158^{0}C, IR-1676 cm^{-1} (νC=O), 1628 cm^{-1} (νC=N), 1580 cm^{-1}(νN=N), 1273 cm^{-1}(νC-O). Anal. Cald. for $C_{23}H_{16}N_4O_3S$, C 64.47%, H 3.76 %, N 13.08% found C 63.18%, H 3.68%, N 12.89%.

Structure of the molecule was tentatively fixed as given in Figure 1 on the basis of elemental analysis, IR, UV and ^{1}HNMR spectral studies.

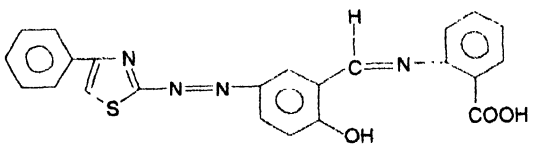

Figure 1. Structure of ligand

The XRD spectra was recorded on Philips PW 3710 diffractometer attached to a digital computer along with graphical assembly in which CuKα radiation source connected with the tube Cu-Ni 25 kV/20 mA was used.

The X-ray diffraction pattern (XRD) of 2-[2′-hydroxy salicylidene-5′-(4″-phenyl 2″-thiazolylazo)] benzoic acid (Figure 2) records thirteen reflections between 10^0 and 80^0 (2θ) with maximum reflection at $2\theta = 17.151^0$ corresponding to a value of $d = 5.164$Å.

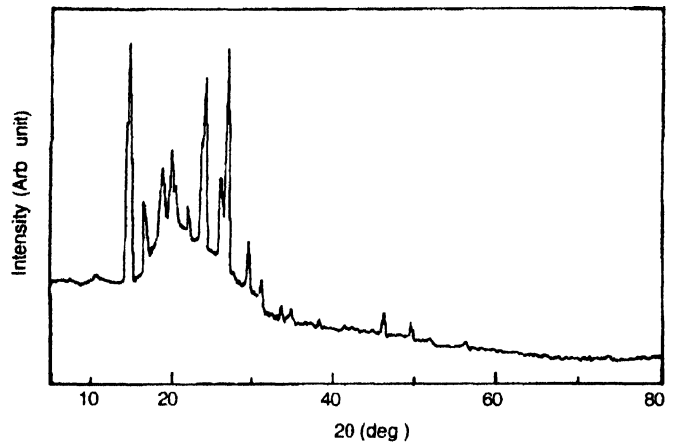

Figure 2. X-ray diffractogramm of ligand.

The X-ray diffractogram with respect to the prominent peaks have been indexed by using computer software by trial and error method keeping in mind the characteristics of various symmetry system till a good fit could be obtained between observed and calculated values of d and Q. The unit cell parameters were calculated from the indexed data refined by weight fraction method. Such refined parameters were used for finding out space group. The method also yielded *hkl* (Miller indices) values. The relative intensities corresponding to prominent peaks have been calculated and are shown in Table 1.

Table 1. X-ray data of 2-[2′-hydroxysalicylidene-5′-(4″-phenyl 2″-thiazolylazo)] benzoic acid

Peak No.	2θ degree	d_{obs} Å	d_{cal} Å	Q_{obs}	Q_{cal}	*h k l*	*RI* (%)	$\delta(Q)x$ 10^4
1	17.151	5 164	5.157	0.0375	0 0376	0 0 2	100.0	2.0
2	18.106	4 895	4 903	0 0417	0.0416	0 1 2	33.1	2.0
3	20.213	4.389	4.385	0.0519	0.0520	2 3 0	28.4	3.0
4	22.119	4.015	4 036	0.0620	0.0614	2 3 1	17.6	3.0
5	23.929	3.716	3.727	0.0724	0.0720	3 3 0	80.8	3.0
6	26.459	3.366	3.360	0.0883	0.0886	0 1 3	91.3	3.0
7	28.312	3.149	3.153	0.1008	0.1006	0 2 3	25.4	3.0
8	34.225	2.618	2.623	0.1459	0.1454	3 5 1	8.3	4.0
9	35.673	2.515	3.513	0.1581	0.1584	1 1 4	6.8	4.0
10	38.508	2.336	2.341	0.1833	0.1824	2 2 4	3.2	5.0
11	46.844	1.938	1.937	0.2663	0.2664	2 5 4	2.9	5.0
12	50.302	1 812	1.817	0.3044	0.3030	1 4 5	3.2	6.0
13	54.747	1.675	1.687	0.5970	0.5928	4 5 5	1.8	6.0

A comparison of values of d and Q for the present ligand shown in Table 1, reveals that there is a good agreement between the calculated and observed values of d and Q on the basis of assumption of tetragonal structure. The structure yields values for lattice parameters $a = b = 15.811$ Å, $c = 10.314$ Å and unit cell volume $V = 2578.37$ Å^3. In conjunction with such cell parameters, the condition [12, 13] such as $a = b \neq c$ and $\alpha = \beta = \gamma = 90^0$ required for the sample to be tetragonal were tested and found to be satisfactory. Hence, it is concluded that the compound under study has tetragonal structure [14, 15].

The experimental value of density of the sample was determined by using specific gravity method, which further enabled to calculate the volume of unit cell. The number of atoms (n) per unit cell were calculated by using equation ($\rho = nM / NV$) and was found to be 1. With this number theoretical density was fixed. When experimental value of density of the sample is compared with the theoretical density value it was found that there is good agreement within the limits of the experimental error. The other parameters such as pore fraction packing fraction, particle size, radius of atom were then calculated The space group and point group of the sample were noted from international Table for X-ray Crystallography [16] These values are presented in Table 2.

Table 2. X-ray parameters of 2-[2′-hydroxy salicylidene-5′-(4″-phen 2″-thiazolylazo)] benzoic acid

Structure	Tetragonal
Space group	P_4/nmm
Laue group	$4/m$
Point group	$4/mmm$
Symmetry of lattice	Non-primitive
Lattice parameters	15.811Å
	10 314Å
Bond angles	$\alpha = \beta = \gamma = 90^0$
Vol. of unit cell	2578.37Å^3
Radius of atom	6 846 Å
Vol. of atom	1343.32 Å^3
Packing fraction	52.09 %
Density p (Experimental)	0.259 g cm^{-3}
(Theoretical)	0.276 g cm^{-3}
Pore fraction	29.73%
Thickness of particle	231.64 Å

The particle size of the sample was calculated by using an equation $t = 0.9\lambda / B\cos\theta$, where λ is wavelength of X-ray radiation in Å, B is the half angular width in radian and θ is

Bragg's diffraction angle. For the determination of particle size, the corresponding peak was enlarged for better accuracy in measuring the half width and then particle size of the sample was calculated. These parameters can distinguish between natural particle size due to broadening effect. This was done by plotting a graph of $B\cos\theta$ *versus* $\sin\theta$. The nature and behaviour of these values are presented graphically in Figure 3.

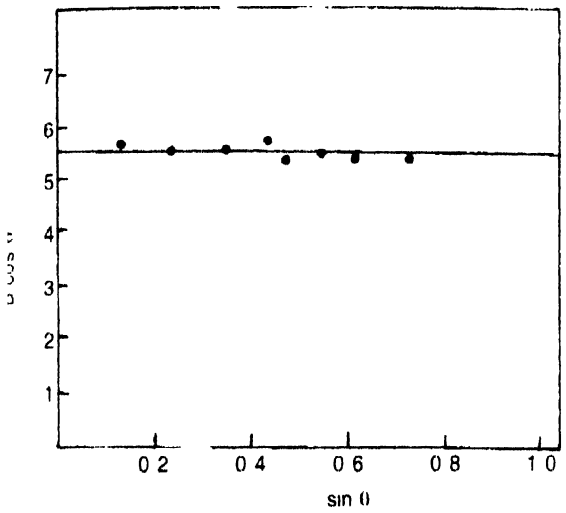

Figure 3. Analysis of homogeneity

A plot of $B\cos\theta$ *versus* $\sin\theta$ was found to be straight line, parallel to X-axis indicating absence of any strains caused by inhomogeneous lattice distortions and compositional fluctuations. Hence, present sample seems to be homogeneous with respect to the particle size distribution.

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